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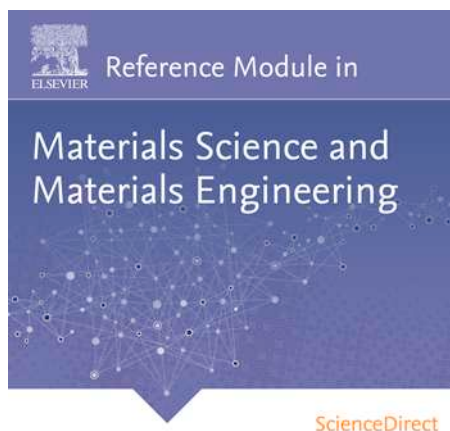
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Effect of Bipolar Plate Materials on Performance of Fuel Cells

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1 Introduction

The recent increase in world population has resulted in high demand of energy. Fossil fuel continue to dominate the energy industry, but unstable prices of fossil commodities coupled with other factors has compelled the research community to consider other alternative to fossil products. The reliance of fossil fuel as a means of energy generation has negative effect on the environment. Recent climate change is attributed to the dependency on fossil products as energy generation medium. Renewable energy sources are today considered as a key replacement of fossil product in futuristic terms. They are often highly abundant with no or less emissions of toxic and harmful substances into the environment. During off peak periods, most renewable energy systems still produce power which goes to waste due to lack of enough energy storage mediums or technologies. These losses affect the running cost of most renewable energy systems prompting the need for new and efficient method of storing these excess energies. Electrolyzers as well as electrochemical device are today viewed as the remedy to these challenges. Excess energy produced during off peak times dissociate water molecules to hydrogen and oxygen via electrolytic process. Using an electrochemical device (e.g., Fuel cell), the hydrogen can then be used to generate electricity for other applications when the need arises. This important application of fuel cells are contributing factors leading to the sudden surge in research conducted for the development of fuel cells. They are friendly to the environment with less or no release of harmful substances into the environment [1]. The research community is currently performing several experiments to reduce the overall carbon dioxide emissions into the atmosphere. Several countries have initiated policies that seeks to hasten the accomplishment of the hydrogen age with the recent Paris Climate Accord being a practical example [2]. There are several kinds of fuel cells but the PEM Fuel cells has currently become a keen research area because of their operational characteristics and material composition. They are very conducive for portable applications and automotive purposes. Proton Exchange Membrane fuel cells functions between temperatures of 60–80°C [3]. The main reactive substances for PEMFC are hydrogen and oxygen/air. The byproduct of the electrochemical reaction is heat and water. Fuel cells have three main parts. The components in a fuel cell are MEA, current collectors and the BP. Weight of the fuel cell is determined by bipolar plate material composition. More than 80% of the fuel cell mass is attributed to the BP while nearly 50% of fuel cell prices is determined by the price of the BP [4–6]. The reactive substance enters the cell via the BP. Distribution of reactive substances on the catalyst layer uniformly is determined by the bipolar plate. Removal of excess heat and water from the cell is controlled based on the nature of the bipolar plate [7]. Electrons released after electrochemical reaction converge on the bipolar plate. Using current collectors, these negatively charged ions then flow via any external circuit connected to the fuel cell. Due to the reactive gases being volatile, the bipolar plate serves as a seal for the fuel cell to prevent the easy escape of the reacting species [6]. Development of fuel cell BP is becoming a critical aspect of research in the fuel cell industry. Today, materials that are less expensive, easy to machine and easily accessible are being considered via experimental investigation for

manufacturing of fuel cell BP. The types of materials used in the production of bipolar plate is categorized into electro graphite, metals and polymers [7]. The types of materials used in manufacturing BP for PEM fuel cells have been reviewed by other researchers [8]. Properties of some materials for manufacturing BP was also reported by Wang *et al.* [8]. A combination of some of these chemical and physical characteristics of these materials have resulted in the evolution of other novel materials suitable for PEM fuel cell bipolar plate production. This investigation explores some of these novel materials in terms of their performance on fuel cells based on their individual physical characteristics. The Department of Energy, US, stipulates that for fuel cell bipolar plate to be suitable for automotive applications and portable applications, they must have excellent electrical and thermal conductivity. Again, their permeability must be good. The BP must further withstand shocks. In terms of mechanical strength, they must not break easily. When exposed to harsh environmental conditions, bipolar plates should be able to resist any form of corrosion. The flow plate should finally be cheap and affordable. The electrical conductivity should be more than 100 S cm^{-1} as well as the interfacial contact resistance being less than $30 \text{ m } \Omega \text{ cm}^2$ [9–15]. Their stability chemically in slightly acidic water pH should also be more than 4. The corrosion resistance should be less than $16 \text{ } \mu\text{A cm}^{-2}$ [15]. Their thermal conductivity must exceed 10 W(m K)^{-1} . It must also be less permeable to hydrogen and oxygen ($2 \times 10^{-6} \text{ cm}^3(\text{cm}^2 \text{ s})^{-1}$). It is required that their flexural strength is more than 59 MPa and their impact strength more than 40.5 Jm^{-1} [16]. Traditional fuel cells often have their bipolar plate made up of graphite. This is because graphite allows the easy flow of electricity and heat. Again, the chemical stability of graphite is good. Graphite as a material has some limitations as well. They are generally expensive and have high volume, reducing their viability for commercial purposes. Today, materials that are cheap with less volume is being investigated by researchers around the world to produce BP [17,18]. Mechanical strength for graphite is low and sometimes tedious working with graphite. This implies that manufacturing BP using graphite is not economical hence increase the overall cost of the fuel cell [19–23]. These setbacks using graphite for bipolar plate production has necessitated the need for the research community to explore other materials like metals. Metals in general have high strength mechanically, support easy flow of electrons, does not allow the easy flow of gas through them, less expensive and can be manufactured easily [24–27]. Stampability and thickness plate reduction of nearly 1 mm are some advantages of bipolar plates made of metals. Several research today is geared towards using stainless steel as material for manufacturing BP. Stainless steel (SS) is made up of a passive film which aid in reducing the possibility of corrosion of the entire material. The passive film has a thickness of 1–3 nm and this is dependent on the steel grade and the environment. The passive film raises the ICR higher between the BP as well as the carbon even though it reduces the rate of corrosion of stainless steel [27]. Stainless steel used in fuel cells go through passivation. The various components in the stainless steel will determine the thickness. Other factors like the composition of the passive film, environment pH, potential being applied and ions in an aqueous state affects the thickness of the stainless steel [28]. Again, the passive film will break down and reform in the slightest change in the environment causing metallic ions to be released leading to contamination. The low cost of polymer carbon composite bipolar plates has attracted a number of researchers into their viability as a bipolar plate material. They also have low weight and their corrosion resistance ability is higher than graphite or metallic bipolar plates [28]. Non – stampability, low electrical and mechanical properties are well known demerits of composites bipolar plates. A novel bipolar plate suitable for fuel cells for commercial applications must have the characteristics of metals, graphite and composites combined together. Today, scientists are adopting various means of making this a reality to reduce corrossions on metals and prevent the passive layer developed on surfaces of metals that leads to low power being generated and increase the possibility of the catalytic and electrolytic layers being contaminated [27]. This review further intends to delve into metallic plates with strong mechanical strength as flow plates for fuel cells. Some parameters like weight and volume must be considered first for any bipolar plate to be accepted for fuel cells. A detailed information on the performance of using bipolar plate made of metals and that made of composite materials is still not covered very much in literature hence the motivation for this review. Other researchers like Tibbetts *et al.* [28] investigated on materials suitable for flow plate. Their investigation covered several kinds of composite properties as well as methods of fabricating a vapor – grown carbon nanofiber/polymer composites. Other researchers also made review papers on coating, material and fabrications of the membrane electrode assembly as well as composite, graphitic and metal flow plates [29]. Material composition as well as processes for the fabrication of flow plates made up of metals has also been investigated thoroughly in literature [30]. The strength and easy electrical characteristics of graphite has also been published by another researcher [31].

2 Bipolar Plates and Their Material Properties

Fig. 1 depicts the various activities in a fuel cell leading to the generation of current. It is made up of anode and cathode backing and membrane electrode assembly. The bipolar plates have several functions. Below are some of the functions of the flow plates. They aid in easy dissemination of the reactive gases on the MEA. BP helps in water management of the fuel cell. They are also good for the separation of individual cell stack and aid in transmitting current from one cell to the other. Thermal management in the fuel cell is also conducted with the help of the bipolar plates [32]. The physical and chemical properties for each material for the manufacture of bipolar plates differ as shown in **Table 1**.

There are other vital physical characteristics of bipolar plate materials and these are: They must have good coefficient of thermal expansion, density and hydrophobicity. According to Borup and Vanderborgh [33] and Cooper [34], in order for a material to be classified as suitable for a BP it must conform to certain characteristics. Electrical conductivity of the material should be very good and have a plate resistance less than 0.01 cm^2 . Again, the material must support the easy flow of heat out of the cell and gas permeability of the material must also be less than $10^{-4} \text{ cm}^3/\text{s cm}^2$. The material should also be corrosion resistant, having a

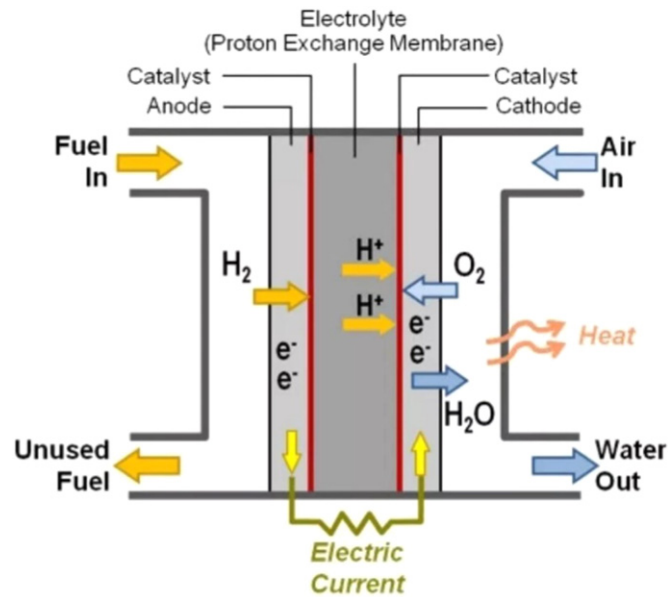


Fig. 1 Electrochemical processes in a fuel cell. Authorization to reproduce obtained from ref Wilberforce, T., Alaswad, A., Palumbo, A., Olabi, A. G., 2016. Advances in stationary and portable fuel cell applications. International Journal of Hydrogen Energy 41 (37).

Table 1 Various characteristic of materials for bipolar plates

Bipolar plate function	Chemical property
Dissemination and maintenance of hydrogen and oxygen as well as residual gases and liquids	Pervious to hydrogen, ability to resist electrochemical deterioration
Conduct electric current	Electrically conductive
Aiding in heat removal	Thermally conductive
Separation of cells in the stack	Mechanical strength

corrosion rate less than 0.016 mA/cm^2 . Strength of the material must also be greater than 22 lb/in^2 and finally the density of the material must be less than 5 gm/cm^3 . Flow plate materials are categorized into Non – metals, Metals and Composite. Fig. 2 shows various materials used as flow plates in cell stacks.

Materials suitable for flow plates are largely classified into metals and carbon-based. The research and development activities and some applications are all geared towards carbon – based flow plates because their densities are very high especially graphite [29]. This is mainly due to the characteristics observed for PEM fuel cells even when operated in bad conditions, but usage of graphite in PEM fuel cells was purposely for laboratory works and stationary applications where the weight of the bipolar plate as well as the volume being low was not considered. Designing of flow channels on these materials is very expensive and the material is also brittle hence discouraging its usage in most terrestrial applications and other applications like the mobile and automotive industry. The transportation field normally prefers cheap mass production processes [26–39]. Metals with the exception of noble metals is mostly preferred especially by the research community due to their easy flow of heat and electricity, low gas permeation, and simple when machining flow channels on them. Their chemical instability in harsh corrosive conditions as found in PEM fuel cells remains the major setbacks for most metallic bipolar plates as this normally leads to their surfaces becoming corroded as well as the formation of thin oxide layer on the surfaces of these metallic materials. This often lead to poisoning especially in the solid polymer electrolyte and even the catalyst layer through the release of corrosion by products (Fe^{3+} , Cr^{2+} , Ni^{2+}). This can cause the ICR between the metallic plates and the GDL layers to increase appreciably leading to depletion in the performance of the cell stack. Several investigations conducted in recent times are geared towards enhancing resistance to electrochemical deterioration as well as interfacial contact resistance of metal flow plates. Some of these strategies involves the usage of a protective layer which is very conductive but very thin on the surfaces of these metals. Different researchers have made several publications on the specific material and processes suitable for the manufacturing of bipolar plates [40–42].

3 Polymer Composite Plates

Another material used as bipolar plate material is composite materials. Composites are very light in weight. It is easy for them to be shaped into any specific size and this makes them suitable for PEMFCs. They are grouped as metals or carbon. The Los Alamos

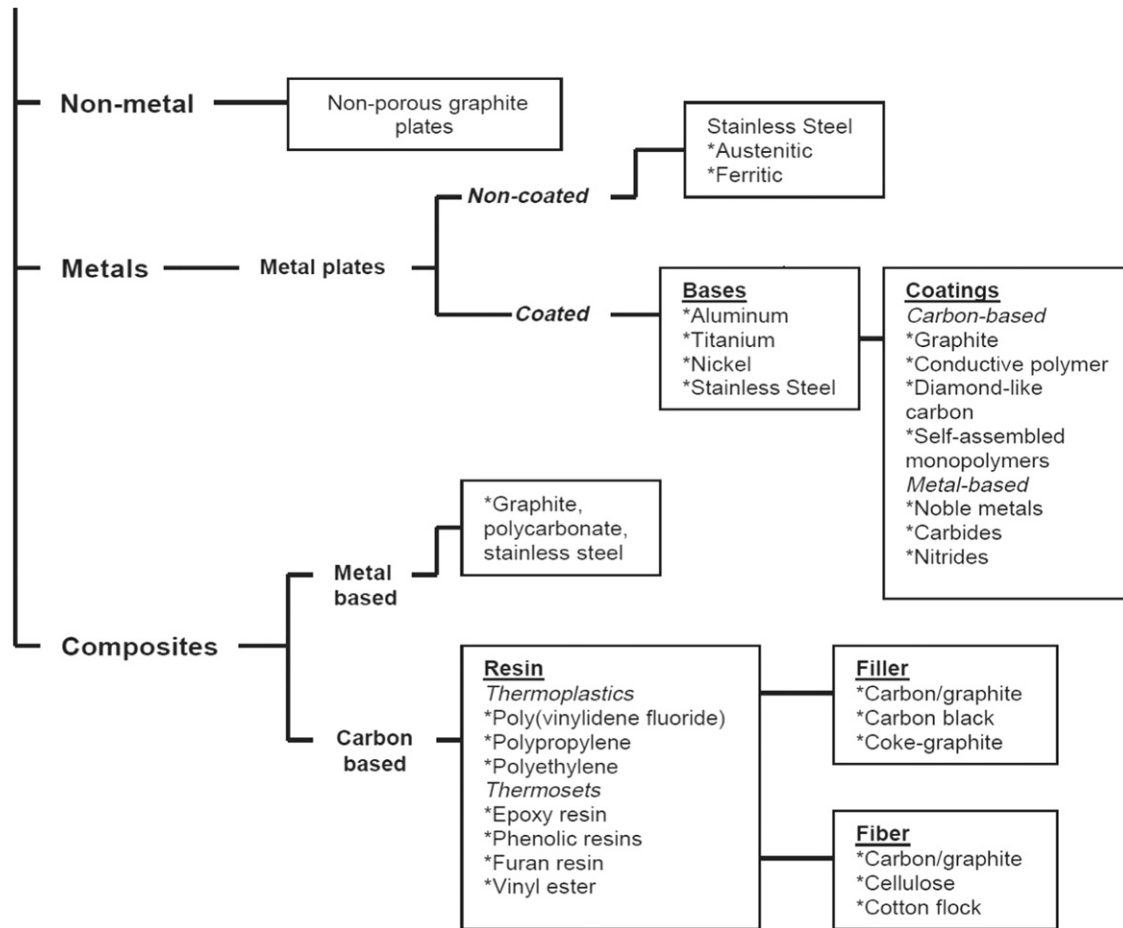


Fig. 2 Flow plate materials for fuel cell stack. Authorization to reproduce obtained from ref. Wilberforce, T., Al Makky, A., Baroutaji, A., Sami, R., Olabi, A.G., 2017. Computational fluid dynamic simulation and modelling (CFX) of flow plate in PEM fuel cell using aluminum open pore cellular foam material. In: Proceedings of the Power and Energy Conference (TPEC), Texas: IEEE. doi:10.1109/TPEC.2017.7868285.

National Laboratory [35] conducted research on a metal based composite flow plate material and the material they developed was made from porous graphite, polycarbonate plastic and stainless steel. Manufacturing porous graphite plate does not require lot of time like that of non – porous graphite plates. It is also not expensive compared to the non – porous graphite plates. It is possible to produce the bipolar plate while the stainless steel and the polycarbonate part provide the impermeability. Stainless steel supports the structure and the possibility of corrosion is curbed using the graphite. Chemical resistance is provided by the polycarbonate and can be transformed into any specific shape to form the gasket as well as the manifold. The plate that was layered showed a better option in terms of stability and the price of the material. The possibility of using composite made of carbon as flow plate in cell stacks has also been investigated. The usage of thermoplastics or thermosetting is one method of producing carbon composite bipolar plates. There has been a major progress in using graphite – polymer composite materials as bipolar plates [43–46]. The manufacturing of materials that is very conductive but made of composite and having excellent properties as well as easily produced commercially for flow plates were all investigated [47]. Another researcher also concluded in his report that the long – term performances of carbon composite flow plates could be likened to graphite. Heinzel *et al.* [38] also reported that there is the possibility of developing a flow plate based on thermoplastics and carbon compounds. A vinyl ester – graphite composite bipolar plate has also been developed by Kuan *et al.* [39] and this involves a bulk molding compound approach with characteristics same to graphite plates. Some companies like DuPont and ICM Plastics are well known for the sale of polymer – graphite composite flow plates [48–57]. It must also be noted that polymer composite material for bipolar plate usually comes as either a polymer or filler as reinforcing material. Fig. 3 shows an example of composite based flow plate material.

3.1 Polymers

Thermoplastic and thermoset can be used to manufacture bipolar plates [35]. The production of bipolar plates need large proportions of fillers irrespective of the nature of the polymer and this usually leads to wetting problems [43]. The polymer should be able to wet the fillers provided the distinction between the fillers and polymers in terms of their surface energies are negligible

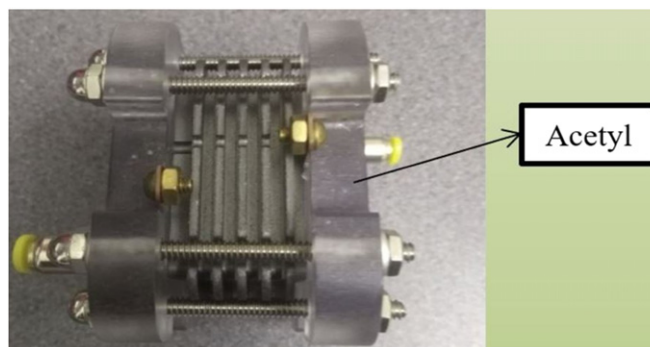


Fig. 3 PEMFC made of a composite/polymer bipolar plate. Authorization to reproduce obtained from ref. Wilberforce, T., El-Hassan, Z., Khatib, F.N., *et al.*, 2017. Modelling and simulation of proton exchange membrane fuel cell with serpentine bipolar plate using MATLAB. International Journal of Hydrogen. doi:10.1016/j.ijhydene.2017.06.091.

as this will result in an increase in the concentration of the fillers. According to research performed by Dhakate *et al.* [44] polymers with polar groups helps the conductive path, therefore the flow of electricity in the polymer increases appreciably as well [44,46]. There are two types of polymers suitable for bipolar plates. These are thermoset and thermoplastic polymers [35,47].

3.1.1 Thermosets

Thermosetting have high strength compared to thermoplastics, ability to resist creep and low mechanical strength [46]. Thermosetting break easily compared to thermoplastics. At higher temperature conditions beyond 120°C, thermosets can maintain their thermal and dimensional stability compared to thermoplastics. Curing process is usually initiated at higher temperatures than the glassing temperature but the viscosity of thermosets is lower at these conditions compared to thermoplastics. These characteristic properties of thermosets are some main reasons for their easy flow of electricity property, mechanically strong as well as reduced porosity of thermoset composites. Different investigations conducted recently is aimed at determining other alternative resins for composite bipolar plates. From literature, three types of thermosets have been thoroughly discussed. These are epoxy [58,59], phenolic [60–64] and vinylester [46] resins. Some of the thermoset resins at room temperature are liquid example the vinylesters found in styrene [65–69]. Other resins must be dissolved in a solvent. Other resins come as either solids or liquids example Epoxy. They come as solid powder shape and even a hardener [69–71]. The last resin that is phenolic are classified into two, that is, resole and novolac [68]. A reaction of formaldehyde and excess amount of phenol with acid catalyst speeding up the chemical reaction leads to the production of novolac [69]. Resole on the other hand is formed by reacting phenol with excess amount of formaldehyde with a base serving as the catalyst. Another agent is need when using novolac resin to aid in curing reaction completely. Hexamethylene tetramine which has methylol group is the agent often used but there is no special agent needed for resole [69]. Polymers allow different processing methods to be applied on them because they come in different forms (Power or liquid). Liquid resins allow the addition of fillers in higher contents in the composite. Solvent is not needed when the resin is in the form of a powder and this makes molding it very difficult.

3.1.2 Thermoplastics

Research work being carried out in fuel cell using thermoplastics for the bipolar plates is also becoming another area of research [72–76]. These materials use fewer amount of fillers so they sometimes look unattractive and less competitive with the other types like the thermosets because they are highly viscous but a shorter cycle time and solvent free process can help mitigate this challenge. Polypropylene is the common and most acceptable type of thermoplastic used as bipolar plate [77–82]. Polypropylene is cheap [83], and it has excellent processing conditions as well as mechanical properties [84]. Another material considered for thermoplastics is polyvinylidene fluoride (PVDF) [80,81]. It does not allow easy penetration of other reactant gases, chemically not reactive, mechanically strong as well as able to resist moisture [82,83]. Other research on polyphenylene sulfide (PPS) has also been conducted because its mechanical properties are good and can be prepared using filler with high contents [84–89]. Polyethylene [87], polyether ether ketone [88], polyethylene terephthalate (PET), polyphenylene oxide [89], nylon [90] and liquid crystalline are some well-known thermoplastics used for bipolar plates [91]. During curing reactions, thermosets allow some gases to escape. Some of these gases are hydrogen, ammoniac and water vapor. The gas pores are usually preferred to be closed and that can only be achieved when the composite is kept under high pressure during its preparation and this also aid in the release of the gas being produced. Using differential scanning calorimetry (DSC) and Thermo-Gravimetry analysis (TGA) are means that can help in the easy specification of the time and temperature delay. There are no curing reactions for thermoplastics. The die where the thermoplastic composite is kept must be cooled below glassing temperature of polymer for thermoplastics to attain a stable state.

3.1.3 Method of molding

The slurry [92], Wet lay (WL) [93], solid state shear pulverization [94], hot compression (HC) [95–98] and the injection molding (IM) [99–101] are some common means of producing composite bipolar plates. Higher electrical and thermal conductivity is obtained when

the hot compression molding method is applied. There is also good dimensional stability using this approach. In the injection molding method, it is impossible to keep the die at such high operating conditions (temperature) with the pressure also being constant, but the hot compression method allows the die to be maintained. In thermosets polymers, keeping a specific temperature and pressure is important to eliminate the gases released during curing hence reducing the porous nature of the composite. A major disadvantage of the IM method is the maximum filler composition added during formulation process is less. The rationale behind is because low viscosity is required to support the easy flow of the material. Conditions during the processing and the direction of the flow in the mold determines the physical characteristics of the composite material. The position of fillers precisely along the direction of the flow for the IM method is many compared to that of compression molding. Materials are sometimes wasted during injection molding especially in the single or double extruder die compared to the compression molding. Till date, the hot compression approach is the well-known strategy for the production of bipolar plates for thermoset composite bipolar plates.

3.1.4 Fillers

All polymers have the characteristics of an electrical insulator hence their ability to conduct electricity is achieved through the addition of conductive fillers. These fillers are sometimes metallic conductors or derivatives of carbons. A number of research in literature are centered around carbon fillers even though metallic conductors are also explored partially as well [101]. The combination of metals and a polymer has its own challenges. The high density of metals coupled with their low corrosion resistance are two main issues that discourage the usage of metals in composite bipolar plates particular among the research community. The popular carbon fillers used for the manufacturing of flow plates are Graphite (G), Expanded Graphite (EG) and carbon fiber (CF) as shown in Fig. 4.

3.1.5 Non-porous graphite

Graphite remains one of the most popular materials suitable for fuel cell flow plates. It comes either as natural or synthetic. This type of material has good chemical stability and performs well when used in a fuel cell. The resistivity of graphite is very low, making it yield high power after electrochemical reaction. It is quite expensive and its mechanical strength is also low. Flow channels must also be created on the flow plates and this is done by machining the channel design on the plates [103]. Scientists today are considering other alternatives to increase the physical as well as chemical characteristics of fuel cell by improving the material.

3.1.5.1 Graphite

The most common bipolar plate material as mentioned earlier is graphite [86]. Apart from diamond and fullerenes, graphite is often in crystalline form. It has good metallic characteristics like very excellent resistance to corrosion, good thermal and electrical conductivities and other properties like inertness and lubricity. Graphite is considered a type of filler that is micro sized with less specific surface as well as low aspect ratio of one. There is therefore an increase in the mechanical property of graphite. The layers of graphite have no reactive surface group and they are usually structure layers having c – axis lattice normally being 0.66 nm. The morphology of graphite shown in Figs. 4(a) and (4b) captures the fracture surface of polymer composite. Graphite has higher electrical conductivity when compared to other existing types of fillers. They are made up of graphene layers interconnected via weak van der Waals forces shown in Fig. 5.

It implies flow of electricity through plane is smaller than that of in – plane for every graphite particle. The electrical conductivity of graphite is estimated to be 10^4 S cm^{-1} at room temperature [87]. Again, it is highly corrosion resistant but challenging in machining flow channels on them as explained earlier and they are also very brittle hence reducing their suitability for the production of a BP [90]. To lower the brittleness for graphite used as flow plates, they are made to have big thickness which in effect increases the weight of the fuel cell as well as the volume [91]. They also have density of 2 g cm^{-3} which is very low.

3.1.5.2 Expanded graphite (EG)

Expandable graphite is obtained through the intercalation of natural graphite by means of modification using different chemical species. The expandable graphite is first introduced to heat in an oven (muffle) at over 800°C temperature to form the expanded graphite (EG) [90–95]. The usage of microwave irradiation in heating the EG is also being investigated lately because it is environmentally friendly and less expensive alternative compared with the traditional way of heating Expanded graphite. The EG is able to expand and exfoliate almost 200 times when introduced to microwave heat for only 30 s along the c-axis direction [96]. The morphology of pure expanded graphite shown in Figs. 4(c) and 4(d) depicts the fracture surface of expanded graphite composite. High expansion of expanded graphite causes alteration of the spacing within the layers of the graphite causing the density to reduce between 10^{-3} and $10^{-2} \text{ g cm}^{-3}$ while the area as well as the aspect ratio will appreciably increase to $40 \text{ m}^2\text{g}^{-1}$ and 15 respectively. Electrical characteristics tend to do well ($12,500 \text{ S cm}^{-1}$) according to an investigation made by some researchers [92]. Graphite nano platelets are created when the exfoliation is introduced to a solvent. Another investigation also reported that the graphite nanoplatelets are able to attain an electrical conductivity of almost 350 S cm^{-1} which is higher than the electrical properties for bipolar plate applications. The high electrical conductivity of expanded graphite has recently been considered as material suitable for bipolar plate and another factor for their suitability for bipolar plates has to do with their high aspect ratio [93–110]. The high aspect ratio reduces percolation threshold in composite bipolar plate [110,111]. This must however be noted that the mechanical strength tends to decrease whenever there is an increase in filler loading of composite bipolar plates hence it is imperative that an optimization of the filler loading must be carried out using a different filler example CF [110].

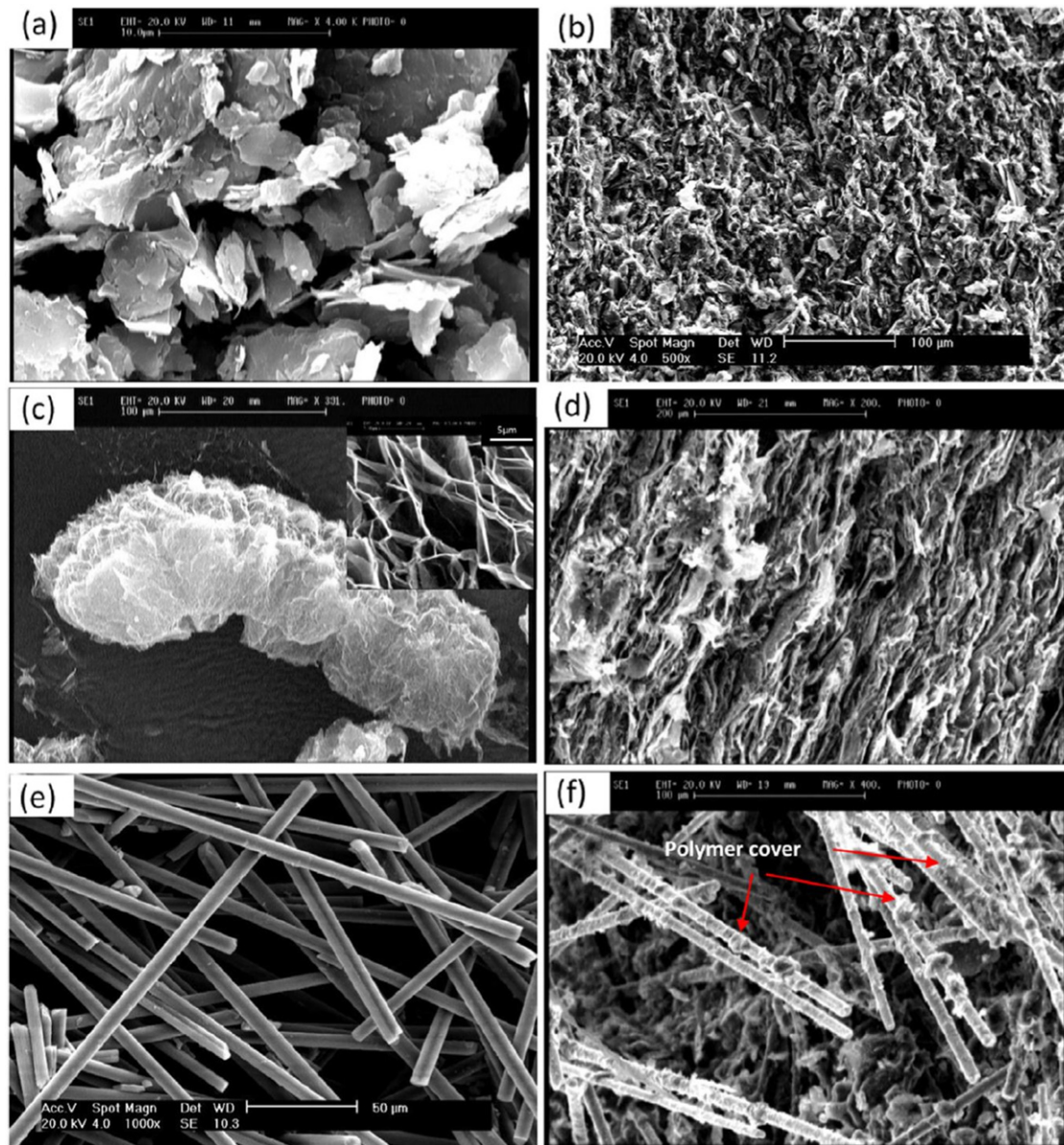


Fig. 4 SEM micrographs images for: (a) Graphite, (b) P/G composite, (c) expanded graphite, (d) P/EG composite, (e) carbon fiber, and (f) P/CF composite. Authorization to reproduce obtained from ref. Wilberforce, T., Alaswad, A., Palumbo, A., Olabi, A.G., 2016. Advances in stationary and portable fuel cell applications. International Journal of Hydrogen Energy 41 (37).

3.1.5.3 Carbon fibers (CF)

They are carbon materials but synthetic in nature as 90% of the material composition is being dominated by carbon. They are formed using various types of precursors such as rayon, pitch and polyacrylonitrile (PAN). The common precursor for the manufacture of high performance polyacrylonitrile carbon fibers is polyacrylonitrile. They are produced by means of pyrolysis of some specific polymeric fibers. The manufacturing process usually involves three stages that is, spinning, stabilization (oxidation) and carbonization. Polymerization of the polyacrylonitrile is the first stage. The material is spun after the polymerization to get the polyacrylonitrile fibers. These fibers are then thermally treated at low temperatures between two hundred and three hundred degrees Celsius but in an oxidative environment where cyclization, dehydrogenation and oxidation are the major reactive processes occurring. The structure of the polyacrylonitrile is changed chemically due to this process hence increasing their stability thermally, for them to maintain their shape and structure during carbonization. Thermoplastic polyacrylonitrile fibers is changed to non – plastic compound due to the stabilization and this is able to resist heat at higher temperatures [111,112]. The polyacrylonitrile fibers being stabilized is then transformed to carbon fibers by means of carbonization that requires heat. Only carbon is retained during this stage. All other elements are eliminated leading to the formation of a graphite like structure [112]. The next stage involves the heating of the carbon fibers under tension between temperatures of 2000–2500°C and 3000°C. This process is

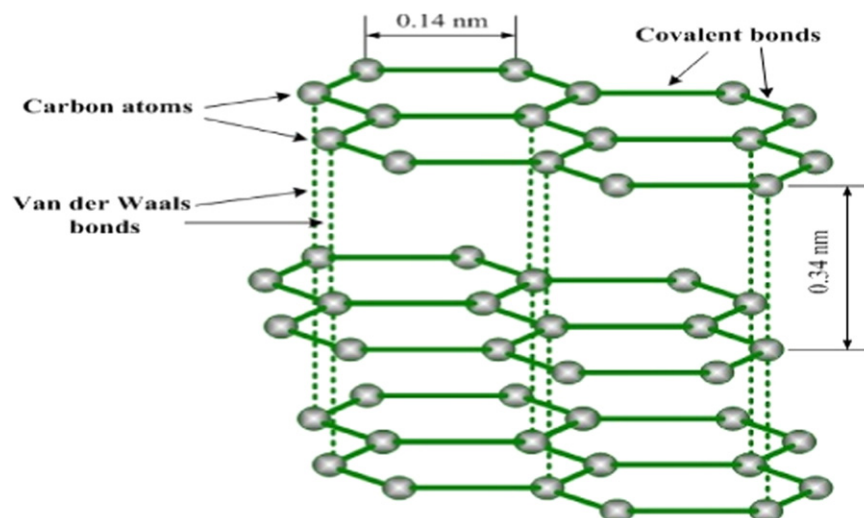


Fig. 5 Weak van der Waals forces showing graphene bonding forces in graphite. Authorization to reproduce obtained from ref. Wilberforce, T., Alaswad, A., Palumbo, A., Olabi, A.G., 2016. Advances in stationary and portable fuel cell applications. International Journal of Hydrogen Energy 41 (37).

carried out in order to graphitize the fibers. The last stage involves using poly matrix to enhance their adhesion by making the carbon fibers undergo surface heat treatments [112]. CF are utilized as composites using light weigh matrix. CF are fillers but they are micronized and again they have high aspect ratio which determines the strength and stiffness of a material hence making them a bit stronger than graphite even at lower intrinsic conductivity [36,37]. The morphology of pure carbon fibers filament is also shown in Fig. 4(e) and that of the fracture surface of carbon fiber composite can also be seen in Fig. 4(f). The strength of the flow plate mechanically tends to increase when carbon fibers are used and this in effect leads to further increment in the conductivity of the flow plate electrically [112–117]. Percolation threshold of the flow plate tends to decrease when the aspect ratio of the carbon fiber is less [117] but the porosity value increases when the aspect ratio increases as well, and this causes the hydrogen permeability to increase. An increase in the filler loading increases this anomaly. Augmenting the wettability of carbon fibers using polymer or a filler with loading of 30 wt% is the only solution to mitigate this challenge [110].

3.1.5.4 Carbon black (CB)

This is an elemental carbon produced synthetically. There are sometimes used as an additive for reinforced rubber products. The process leading to the production of carbon black involves 5 main stages. They are currently made using Furnace or acetylene processes [116]. A reactor is first preheated to a temperature of 800°C before the acetylene gas is introduced. There is an exothermic decomposition of the acetylene at this high reactor temperature. This leads to the production of carbon black surface with temperature exceeding 2500°C but in reality, the formation of carbon black is normally between 800 and 2000°C. Acetylene black have intermediate particle size and also have its crystallinity being fairly high compared to other types of carbon blacks. They equally have high structure but show low reactivity. These characteristics of CB has made them good material selection option for applications that require good electrical and thermal conductivity. CB comes as pellets between 100 and 2 mm and when combined with a polymer, the pellets separates into primary agglomerates 30–100 nm long. This material aid in the improvement of the electrical conductivity even at lower filler loadings. The general nature of the carbon black having high surface area helps it to contact huge amount of polymer leading to the improvement of electrical conductivity even at lower concentration of the carbon black [118]. There is a clear difference between carbon black, graphite and carbon fibers even though they are all made of carbon. Carbon black is made up of aggregates having their configurations complex, quasi graphitic structure and colloidal dimensions [118,119]. The morphology of carbon black is complex. Using CB as bipolar plate material is highly possible but it's low mechanical strength and low electrical conductivity reduces its suitability for bipolar plate needed for commercial purposes [51].

3.1.5.5 Carbon nanotubes (CNT)

The carbon with tubular structure is called Carbon nanotubes. The structure of the tube is normally between 1 and 50 nm in diameter and 1 mm to very small centimeters in terms of length [119]. The aspect ratio of Carbon nanotubes is very large. Today carbon nanotubes are used mainly for multiwall or as single walls for laboratory purposes [120]. The research community is currently turning their attention to carbon nanotubes because their physical characteristics are unique. Carbon nanotubes have their elastic modulus being very large hence they are noted for reinforcing agents. Carbon nanotubes having small diameters exhibits semi – conducting or metallic characteristics but that is dependent on their molecular structure. Carbon nanotubes play a vital function in the catalyst layer for PEMFC, mainly as support sites for the platinum. Carbon nanotubes are generally expensive

hence using them for bipolar plate will exceed the minimum expected cost of bipolar plates being less than $5\$(\text{k W})^{-1}$. There is synergic effect using carbon nanotubes fillers due to their high aspect ratio but this can be curbed if the agglomeration of carbon nanotubes via the polymer is controlled properly. Other research was conducted using filler loading of 1 wt% [121–123]. The possibility of improving the characteristics of composite bipolar plate by means of nano structure filler has also been investigated. This process requires using several vol% of multi wall CNT in graphite – polymer composite bipolar plates. According to research, adding 1 vol% of multi wall carbon nano tubes increases the electrical as well as thermal conductivity for nano composite by nearly 100% [123]. The corrosion current density (I_{corr}) of material made of composite in varying carbon nano tubes weight percentages was less than the DOE standard of $1 \mu\text{A cm}^{-2}$. Formation of multi wall carbon nanotubes agglomerates can lead to depressing the resistance to corrosion as well as the electrical conductivity.

3.1.5.6 Graphene

At very low filler content graphene can still show some good characteristics hence their recent interest by the research community as a suitable material for bipolar plates. Other research has been done using graphene and graphene oxide. Graphene is also used during the manufacturing of nano composites with varying polymer matrices [123–130]. The percolation threshold is even achieved at low filler loading for most graphene-based polymer nano composites. A crystalline flake graphite is formed when several layers of graphene are stack together [124]. Graphene is very light (1 m^2 sheet weighing 0.77 mg) and super conductive electrically. It is also very strong compared to other materials extraordinarily. The production cost of graphene is very high hence reducing their suitability for bipolar plate materials. Graphene was utilized as filler in the bipolar plate material composition according to an investigation carried out by some group of researchers [130]. Characteristics of graphene reinforced composite flow plate was able to meet all these demands hence in terms of conductivity and mechanical characteristics graphene is considered to be more advantageous to use as filler compared to other bipolar plate materials. The limitation of the usage of graphene has to do with the cost of the material.

3.2 Characteristics of Composite BP

Alternative to metal and graphite bipolar plate is the polymer or carbon composite BP. This is because it is cheap, easy to machine flow channels on them, resistant to corrosion and also light in terms of weight [131–136]. The various designs and the kind of material for PEMFC has been studied in detail [23]. They presented current development of bipolar plate using various techniques. Other researchers investigated on conductive thermoplastic blends for injection and compression molding of bipolar plate with the aid of carbon filled PP and PPS [54]. Their research was directed towards the study of the characteristics of BP to 60 wt% loading of the fillers (natural, graphite, conductive carbon and carbon fibers). Another researcher used liquid crystal polymer as binder. The group used Carbon black and Carbon Fibers as fillers for producing the composite bipolar plate. They concluded that the new composite had good mechanical strength and low hydrogen permeability when used as bipolar plate. The electrical conductivity they reported after their investigation was 5.6 S cm^{-1} . The electrical properties of bipolar plate were also investigated to ascertain the impact of some processing factors on their performance [132–147].

The approach utilized was mixing process as well as solution blending. Their investigation also concluded that heating the samples at 100°C for some hours caused a variation in how conductive the samples were electrically but the conductivity they published was only 10 S cm^{-1} . A suggestion was also made in their report, where a third additional conducting component was recommended to give high flow of electricity for the composite bipolar plate. An optimization for the process conditions of compressing molding for PF resin and graphite composite was also investigated by another group of researchers [134,148–169]. Their work showed that the best conductivity as well as the bending strength of the BP they investigated was 142 S cm^{-1} and 61.6 MPa respectively. They generated this result after 1 h from 15% resin content and compression molding at 24°C . They also tried enhancing the mechanical strength of the composite through the usage of nanofillers of carbon nanotubes [170–185]. An increase of the mechanical strength from 50 to 60 MPa for the bipolar plate was achieved through reinforcement of the material with 3% carbon nanotube according to their research. The electrical conductivity tends to decrease as the mechanical strength increases due to the addition of an organic matrix to the carbon – based fillers. It therefore becomes necessary that the two properties are in perfect agreement with each other. Other research groups have also investigated the electric conductivity and strength of phenolic resin, carbon fibers, graphite and enhanced graphite composite [171–185]. They studied the impact of each filler on the various material through the addition of 10–80 wt% of the filler. The synergic impact of two fillers was identified by fabricating double filler and triple filler composites according to their investigations. Their work also led to the development of a triple filler composite made of phenolic resin, 45 wt% of graphite, 10 wt% of enhanced graphite, 5 wt% of carbon fiber and thin carbon fiber cloth shown in Fig. 6.

The flexural strength for this composite from their investigation was 74 MPa , toughness, 39 J m^{-1} , 101 S cm^{-1} was the conductivity determined electrically, thermal conductivity greater than 9 W (m K)^{-1} and porosity less than 5 vol% using this composite yielded maximum power density of 810 mW cm^{-2} . A formula that predicted the conductivity of composites made of polymer electrically was also proposed by another researcher [186].

4 Metals

Metals sheets are also being explored as alternative material for flow plates because metals have excellent mechanical strength, conduct electricity as heat very well and easy to shape to any design for the flow channels. Metal plates are susceptible to corrosion

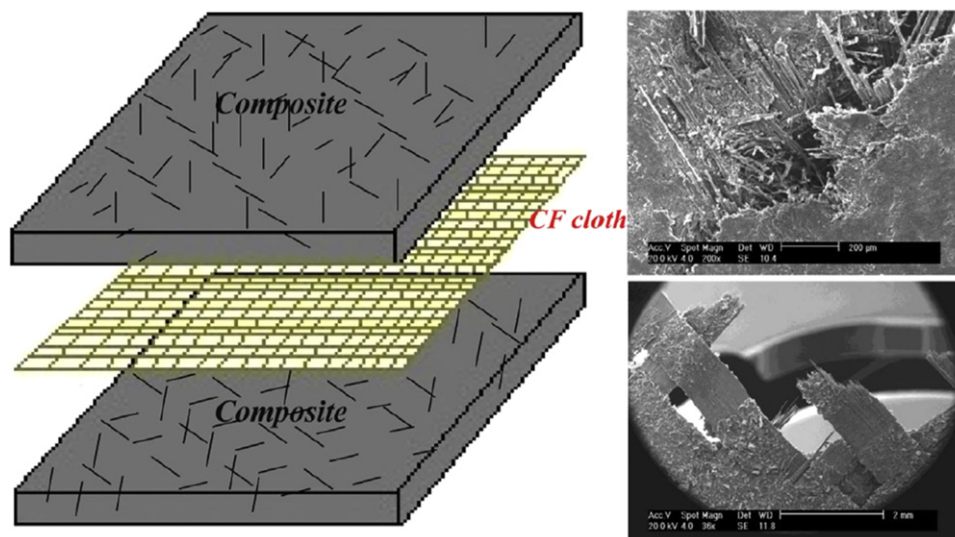


Fig. 6 Diagram showing a triple filler composite. Authorization to reproduce obtained from ref. Wilberforce, T., El-Hassan, Z., Khatib, F.N., *et al.*, 2017. Developments of electric cars and fuel cell hydrogen electric cars. International Journal of Hydrogen 42 (40), 25695–25734. doi:10.1016/j.ijhydene.2017.07.054.

when exposed to a pH of 2–3 and a temperature above 80°C. The metal ions that is dissolved cause poisoning of the fuel cell membrane hence reducing ionic conductivity. The electrical resistance in the fuel cell increases when an area the flow plate becomes corroded and this reduces the performance of the fuel cell. This report reviewed 2 types of metallic plates that is coated and non – coated. These metals include aluminum, stainless steel, titanium and nickel. Their good conductivity with respect to electricity and heat, ability to go through plastic deformation without the material being destroyed, easy to manufacture, gas impermeability as well as mechanical strength makes them very attractive for flow plates. They are generally tough and can resist shocks compared to graphite and composite bipolar plates. They can also be easily fabricated making them advantageous compared to other materials. Metals equally has some well-known disadvantage like being easily corroded when exposed to harsh atmospheric conditions [187]. Corrosion in PEM fuel cells usually happen at the anode and cathode region of the fuel cell. Reduction of the protective metal oxide layer occurs around the anode when exposed to harsh environmental conditions and this leads to hydride being formed and dissolution of the metal in water. Adding water vapor to the hydrogen to keep the membrane humidified is one medium where corrosion could occur in the fuel cell. This again can contaminate the fuel cell, limiting the operational characteristics of the catalytic surface and the fuel cell as a whole. The cathode is the region where the air is oxidized and this also tends to increase the rate of corrosion of the metal bipolar plate increasing the losses and sometimes malfunction of the entire fuel cell prematurely. Coating of the metals has also been investigated by several researchers to reduce the possibility of corrosion [33]. Stainless steel (SS), aluminum, nickel and copper are materials used in the manufacturing of flow plate [24]. Most research conducted is related to Fe – based alloys particularly SS because they are cheap and very abundant. Some metals like stainless steel and titanium are general stable when they are used in fuel cells because they have low pH due to passivation for good corrosion characteristics. Stainless steel and titanium have strong mechanical strength and the gas permeation rate is low [188–201]. Several investigations have been conducted using stainless steel and titanium because even in acidic conditions, titanium and stainless steel still maintain their properties.

5 Conclusion

The work investigated materials for the manufacturing of bipolar plates in cell stacks. Graphite and carbon continue to dominate materials for BP. The cost of fuel cell will reduce after a period of time as the cost of these materials keep reducing from time to time. It implies that bipolar plates are commercially becoming reliable which in effect will reduce the prices of PEM fuel cells as well as also increase their availability on the energy market but the electrical conductivity of graphite still remains a challenge. Middelma *et al.* [47] in their investigation concluded that the conductivity for graphite was nearly 20 S/cm which was well below the target of being greater than 100 S/cm acc. The entire conductivity for DuPonts bipolar plate is between 25 and 33 S/cm. Scientists today are working to produce bipolar plates which are consistent in terms of physical and chemical properties. The automobile industry is encouraging the use of metals as bipolar plates due to metals having small thickness and weight as well as good conductivity both thermally and electrically. Using stainless steel would reduce the cost but non – coated SS from investigation still have some challenge with surface – insulating layer. It therefore becomes imperative that it is coated using a thin coating of a chemically stable and electrically conducting film before it can be suitable for bipolar plates. Several researches is being conducted on coated metal plates and polymer – graphite composites. Despite the fact that there has been good progress made,

researchers are yet to attain long – term reliability and power densities known to usually be the properties of non – porous graphite. It therefore implies that economics, manufacturability and long – term reliability determines the effect of the materials when used as flow plates for fuel cells hence the need for further investigation into this grey area.

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